

Heterogeneous decay of metastable phase on various centers - 1

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Abstract

A system of a metastable phase with several sorts of heterogeneous centers is considered. An analytical theory for the process of decay in such a system has been constructed. The free energy of formation of a critical embryo is assumed to be known in the macroscopic approach. At first all asymptotic cases are investigated and then a general intermediate solution is suggested. All approximate transformations are accomplished with the corresponding numerical estimates and analytical justifications. This is the first part of the manuscript. the second part follows the first one in the e-print archive.

1 Introduction

The kinetics of condensation on various centers which simultaneously exist in the system will be constructed here. The case of condensation of a supersaturated vapor into a state of liquid droplets seems to be the simplest case among the first order phase transitions. Traditionally this case is considered as a model to introduce some new theoretical constructions in description of the first order phase transitions. Ordinary the process of nucleation occurs on dust particles or on heterogeneous centers. A case of heterogeneous condensation was a first object in regular investigations of the first order phase transitions made by Wilson [1]. A first technical device constructed by Wilson, i.e. the famous Wilson chamber was based on the effect of heterogeneous condensation (see also [1]). A problem of the chamber purification is one of actual problems in experimental observations of the homogeneous condensation and the heterogeneous way of nucleation is the most usual way of the droplets formation in nature. So, the case of heterogeneous condensation which will be investigated is very wide spread in nature.

The case of condensation is the most well investigated example of the first order phase transitions. This leading role of the case of condensation was outlined by creation of the classical theory of nucleation by Volmer [2], Becker and Doering [3], Zeldovitch [4] which gave for the first time an expression for the rate of nucleation (i.e. for the rate of an appearance of new droplets), which will be an elementary brick in further constructions. The careful analysis of the classical theory leads to great number of the publications with various reconsiderations of classical expressions. Among them one has to notice the account of the internal degrees of freedom in the embryo made by Lothe and Pound [5], another modifications made by Reiss, Cohen and Katz [6], Reiss [7], Fisher [8]. The application of the density functional theory to the first order phase transition made by R.Evans and D.Oxtoby [9], D.Oxtoby and D.Zeng [10] allowed to put the microscopic (mesoscopic) models for the condensed substance as the base for an expression for the free energy of the critical embryo and for the rate of nucleation. In the publications of Oxtoby and Talanquer [11], Reiss, Tabazadeh and Talbot [12], Reiss, Ellerby and Weakliem [13] - [16] the role of the environment around a droplet is carefully analysed. It is equivalent to some specific choice of the statistical ensemble.

Nevertheless one has to notice that there is no perfect coincidence between concrete theoretical predictions¹ and experimental results. So, this question is still opened in the modern state of investigations. But the mentioned expressions for the nucleation rate reproduce a qualitative behavior of experimental results quite adequately. Moreover, a relative deviation between theoretical predictions and experimental results is very smooth function of parameters.

The mentioned publications allowed to start an investigation of the global kinetics of heterogeneous condensation. The qualitative description of the global evolution during the first order phase transition was initiated by Wakeshima [17] who considered time lags (characteristic times) for condensation. The characteristic time of formation of the droplets spectrum was necessary to ensure a correct experimental definition of the stationary rate of nucleation. After [17] the interest for the description of the global evolution was growing continuously.

The nature and the content of aerosol or heterogeneous particles are so various that different approaches to describe the process of condensation are required. Speaking about the aerosol particles one supposes that these particles are already the supercritical objects of a liquid phase. These objects are growing irreversibly and regularly in time while the objects of a liquid

¹Certainly, one can not check directly some general recipes as to calculate the objects like statistical sums.

phase formed on heterogeneous centers have to overcome the activation barrier. The latter can be done fluctuationally and the process of the supercritical embryo appearance resembles the homogeneous nucleation, but the height of activation barrier is smaller than in the homogeneous case.

Here the supercritical objects of a liquid phase (may be with a heterogeneous center inside) will be called as droplets while the objects of a liquid phase with an arbitrary size and nature will be called as "embryos" or as "particles of a new phase". Very often there is no need to consider the process of the droplets formation because in the system there is a sufficient quantity of aerosol in the system. This case is extracted by the evident simplification that the total number of droplets is already known. Sometimes this case is described as a barrierless formation of droplets. The description of this situation one can see in [18] where this case was completely investigated.

When the activation barrier exists then the total number of droplets is unknown and one has to determine a number of droplets and their size spectrum and has to solve a complex non-linear problem. To solve this problem numerical calculations were presented in [19], [20]. The numerical method of calculations presented in [20] allows to establish in [19] some dimensionless combinations which essentially simplifies the numerical procedure. This simplification gives a way to fulfill some rather complex numerical calculations.

The next step in the development of the global evolution description was the sectional model [21] which simplifies calculations one more time and allows to take into account both nucleation and coagulation. In this publication the process of coagulation isn't described because the probability of this process is very low and it can be observed only a long time after the end of nucleation, i.e. the end of the process of intensive formation of super-critical embryos.

The main difficulty of the nucleation kinetics is a necessity to take into account the exhaustion of a vapor phase due to a vapor consumption by droplets. This exhaustion diminishes the nucleation rate for new imaginary droplets. Sometimes this influence isn't essential and it is shown in [22] that this situation is rather wide spread in laminar flows. In [22] a theory for this case was given and some methods to describe the global evolution were presented. The great importance of the problem of the vapor exhaustion around the droplet was stressed by H.Reiss in [23] where the stationary profiles around droplets were obtained.

To take this influence into account one has to solve a non-linear problem. The simplest way to analyze this problem is to act in frames of some characteristic values of time and space. Namely this way was chosen in [24].

An effect of a heterogeneous centers exhaustion also diminishes the intensity of the new droplets appearance. This effect also has to be taken into account. One has to solve this problem in a self consistent way. The theory for the condensation on one type of heterogeneous centers can be found in [25], where the approximate self consistent solution of the balance equations is given.

Now one has to specify the situation considered in this publication. One has to mention that ordinary in the system there exist several types of heterogeneous centers of different nature. These centers can have different values of the activation barriers under the given value of metastability in the system. Sometimes the difference between centers with neighbour characteristics is so small that one can speak about the quasi-continuous activity of the band of heterogeneous centers. But sometimes the difference in barriers heights between centers with neighbor characteristics leads to their different kinetic behavior.

To show the variety of situations two examples will be given. In the process of condensation on the ions the free energy of the critical embryo depends on the sign of electric charge. As it is shown in [26] the free energy F of an embryo with ν molecules inside can be presented as

$$F = -b\nu + a\nu^{2/3} + c_1\nu^{1/3} + (c_2 + c_3)\nu^{-1/3} + c_0 \ln \nu + const \quad (1)$$

Here and later all energy-like values are expressed in units of the mean thermal energy; a, b, c_0, c_1, c_2, c_3 are some parameters. This formula is valid for the embryo in the state of internal equilibrium, i.e. near the value ν_c of a number of molecules in the critical embryo (corresponding to the maximum of F) and near the value ν_e of a number of molecules in the equilibrium embryo (corresponding to the minimum of F). All values at $\nu = \nu_c$ will be marked by the lower index c and all values at $\nu = \nu_e$ will be marked by the lower index e . It is necessary to notice that a, b, c_0, c_1, c_2 don't depend on the sign of the charge q and a value of c_3 is proportional to q . Since $\nu_e < \nu_c$ then the height of activation barrier $\Delta F = F_c - F_e$ depends on the sign of q . So, in presence of radiation one has two sorts of centers (positive and negative) with different heights of activation barriers, i.e. with different activities of heterogeneous centers.

The spectrum of the sizes of heterogeneous centers as the solid balls with a weak interaction between the heterogeneous center and a liquid phase leads to the spectrum of activities of heterogeneous centers. In the simple model with the passive nuclei one has to add to the surface term the number of the molecules imaginary contained in the volume occupied by the nuclei. The free energy of the critical embryo is given by

$$F = -b\nu + a\left(\nu + \frac{4\pi r^3}{3v_l}\right)^{2/3} + const \quad (2)$$

where r is the radius of a heterogeneous center, v_l is the volume occupied by a molecule of a substance in a liquid phase and $F_e = const$. A continuous spectrum of sizes of heterogeneous centers initiates a continuous spectrum of the activation barriers heights.

As the result two different situations can take place - the situation with several types of centers and the situation with continuous variation of the properties of centers. Any spectrum of activation barrier heights can be split into several continuous parts (may be also like δ -functions) which will be considered as the "types" of heterogeneous centers.

Now one has to specify external conditions. Kinetic description of the condensation process implies external conditions to be known. There are two characteristic types of external conditions. The first one is the external conditions of the decay type - until some moment the system is in the stable state and then rather rapidly due to the action of external forces the initial phase becomes metastable. Then the external action stops. This type of conditions is deeply connected with typical conditions in the chamber experiments. Investigations of the condensation kinetics [17] were started in this situation.

The second typical conditions are conditions of the dynamic type. The action of external conditions gradually creates metastability but a rapid growth of a vapor consumption by droplets at some moment begin to compensate an action of external conditions, which doesn't stop. The rate of a vapor consumption grows so rapidly that the power of metastability falls and the process of nucleation stops. This situation is described in [25] for a system with one type of heterogeneous centers.

Why the situation of decay on several types of heterogeneous centers requires a special consideration? For the condensation on one type of heterogeneous centers one can see a certain

analogy between two mentioned types of external conditions. This is explained by the evident notation that in both situations the intensive formation of new droplets occurs near some characteristic value of the power of metastability². During the nucleation on different sorts of heterogeneous centers in the situation of decay the characteristic value of the power of metastability is one and the same for all types of centers and in the situation of dynamic external conditions the characteristic value of metastability is determined separately for every type of centers. This explains why one has to use different methods for different specific situations of heterogeneous condensation on many types of centers. In the current publication the situation of decay for heterogeneous centers with arbitrary activities will be analyzed.

One has to study the period of the intensive formation of the droplets, i.e. the nucleation period. The further evolution is described analogously to the condensation on one type of centers.

The following physical assumptions to formulate the model will be used: the thermodynamic description of the critical embryo; the random homogeneous space distribution of heterogeneous centers; the homogeneous external conditions for temperature and pressure; the high (in comparison with one thermal unit) activation barrier³; the absence of thermal effects. One can see that these assumptions are rather natural. The unit volume is considered.

According to [27] the condensation equations in the general conditions are analogous to the case of the free molecular consumption of the vapor and namely this case will be studied.

A homogeneous character of a distribution of heterogeneous centers implies that in a characteristic space region there is a big quantity of heterogeneous centers of every type⁴. The characteristic space size of this region is determined as a mean distance of the diffusion relaxation during the whole nucleation period. For the pure free molecular regime of droplets growth the characteristic size is the size of a system.

The total number of the heterogeneous centers is assumed to be constant in time. This is also quite natural because the period of nucleation is relatively short in comparison with other characteristic times of the condensation process (except the time of relaxation to the stationary state in the near-critical region).

Since the most interesting characteristics of this process are the numbers of droplets on the different types of centers, the accuracy of the theory will be estimated by an error in this value.

2 Kinetic equations

The total number of heterogeneous centers will be marked by $\eta_{tot\ i}$, where i corresponds to some sort of the heterogeneous centers. The absence of this index points that the formula is valid for an arbitrary sort of heterogeneous centers. The numbers of the free heterogeneous centers which aren't occupied by the super critical embryos are marked by the value of η_i .

One can define the neighbor sorts of heterogeneous centers as the centers with neighbor values of the activation barriers heights. When the difference in the activation barriers heights for the neighbor sorts is many times less than one thermal unit one can speak about the quasi

²This value is determined by external conditions.

³The theory without the heterogeneous activation barrier is much more simple.

⁴For the quasi continuous spectrum of activities the different type means that the difference of the activation barrier height is greater than one thermal unit.

continuous spectrum of activities of heterogeneous centers. The latter doesn't mean that the total variation of the activation barriers heights is less than one thermal unit.

It is convenient to introduce the characteristic of "activity". One can define "an activity of a heterogeneous center" as some parameter w which is proportional to a deviation in the height of the activation barrier

$$\Delta F(w) = \Delta F|_{w=0} - \lambda w \quad (3)$$

with some positive parameter λ . The base of decomposition ($w = 0$) is now an arbitrary value and will be chosen later to simplify formulas.

A total number of heterogeneous centers with a given activity w will be marked by $\eta_{tot}(w)$. Naturally $\eta_{tot}(w)$ is a smooth function of w . Then the neighbor sorts of heterogeneous centers have neighbor rates of the droplets formation⁵.

A density of the molecules in the equilibrium vapor is marked by n_∞ , a density of the molecules in the real vapor is marked by n . A power of the metastability will be described by the supersaturation

$$\zeta = \frac{n - n_\infty}{n_\infty} \quad .$$

Every droplet can be described by the linear size $\rho = \nu^{1/3}$. Due to the free-molecular regime of the vapor consumption

$$\frac{d\rho}{dt} = \zeta \alpha \tau^{-1} \quad , \quad (4)$$

where α is the condensation coefficient and τ is some characteristic collision time easily obtained from the gas kinetic theory.

The following statements can be analytically proved:

- The main role in the vapor consumption during nucleation is played by the super critical embryos, i.e. by the droplets.
- The quasi stationary approximation for the nucleation rate is valid during the nucleation period.

Justification of the second statement uses the estimate for the times t_i^s of the establishing of the stationary state in the near-critical region which can be found in [4] (for heterogeneous case the consideration is similar). They have to be many times less than duration of nucleation period. There may exist some big times t_i^s . They correspond to big values of ν_c . It means that $\Delta_i F$ are huge and these sorts of heterogeneous centers are passive and out of intensive nucleation.

The characteristic time t_* necessary as the base for decompositions will be the time of beginning of nucleation. The values at the moment t_* will be marked by the lower index *. One can choose the zero point of the time axis as t_* and introduce the frontal size z according to

$$z = \int_0^t \zeta \alpha \tau^{-1} dt' \quad . \quad (5)$$

Until the coalescence eq. (5) ensures the growth of z in time and can be inverted

$$t(z) = \int_0^z \tau \alpha^{-1} \frac{dx}{\zeta(x)} \quad . \quad (6)$$

⁵The sort of the droplets means the sort of the heterogeneous centers.

All functions of time become the functions of z and the relative size $x = z - \rho$ can be introduced. During the whole evolution the droplet has one and the same value of the variable x . Considering the value $t(x)$ as the moment when the droplet with a given x has been formed (as a droplet, i.e. it begins to grow irreversibly) one can consider all functions of time as functions of x or z . The variables x and z become equivalent. Hence, one can see that the kinetic equation in the supercritical region is reduced to the fact that every droplet keeps the constant value of x . To reconstruct the picture of evolution one must establish the dependencies $t(z)$ and $\zeta(x)$.

The argument ∞ will mark the total values of the characteristics formed during the whole nucleation process. Practically immediately after creation of metastability the value of the supersaturation falls down to

$$\Phi_* = \zeta(0) - \frac{\sum_i \eta_{tot\ i} \nu_{e\ i}}{n_\infty} . \quad (7)$$

During the period of the essential formation of the droplets one can assume that the value $\nu_{e\ i}$ is constant and take it at $\zeta = \Phi_*$. In initial approximation $\nu_{e\ i}$ can be taken at $\zeta = \zeta(0)$.

One can analytically prove during the period of nucleation on some given sort for the variation of the supersaturation

$$|\zeta - \zeta_*| \leq \frac{\Phi_*}{\Gamma_i} ,$$

where

$$\Gamma_i = -\Phi_* \frac{d\Delta_i F(\zeta)}{d\zeta} \Big|_{\zeta=\Phi_*} . \quad (8)$$

The same is valid for all sorts of centers when Γ_i is substituted by $\min_i \Gamma_i$.

Let f_{*i} be the amplitude value of the distribution f_i of sizes of heterogeneously formed droplets measured in units of n_∞ . According to the second statement the value of distribution equals to the stationary distribution which is the stationary rate of nucleation divided by the droplets rate of growth and by the value of n_∞ . Then the stationary distribution f_i can be easily calculated by the following known formulas [4]:

$$\frac{J_i \tau}{\alpha \zeta n_\infty} = f_i = \frac{W_c^+ \exp(-\Delta_i F) \tau}{n_\infty \pi^{1/2} \Delta_{e\ i} \nu \Delta_{c\ i} \nu \zeta \alpha} \eta_i \equiv f_{\zeta\ i} \eta_i , \quad (9)$$

where W^+ is the number of the molecules absorbed by the embryo in a unit of time, $\Delta_e \nu$ is the characteristic width of the equilibrium distribution

$$\Delta_{e\ i} \nu = \sum_{\nu=1}^{\nu=(\nu_c+\nu_e)/2} \exp(-F(\nu))$$

and $\Delta_{c\ i} \nu$ is the half-width of the near-critical region⁶

$$\Delta_{c\ i} \nu = \frac{2^{1/2}}{\left| \frac{\partial^2 F}{\partial \nu^2} \right|_{\nu=\nu_c}^{1/2}} .$$

For the majority of types of heterogeneous centers the following approximations of the nucleation rates J_i are valid during the nucleation period

$$J_i = J_i(\eta_{tot\ i}, \Phi_*) \exp\left(\Gamma_i \frac{(\zeta - \Phi_*)}{\Phi_*}\right) \frac{\eta_i}{\eta_{tot\ i}} . \quad (10)$$

⁶Here the steepens descent approximation is used.

The validity of these approximations can be easily justified for monotonous interaction between the center and the molecules of the substance which is weaker or equal than the function reciprocal to a space distance. For the centers with another interaction this approximation has to be checked directly.

The total number of molecules in droplets formed on the sort "i" is marked by $n_\infty g_i$. To simplify the formulas $\theta_i = \eta_i / \eta_{tot\ i}$ will be used.

Using the conservation laws for the heterogeneous centers and for the molecules of the substance one can get for g_i, θ_i the following equations⁷

$$g_i = f_{*i} \int_0^z (z-x)^3 \exp(-\Gamma_i \frac{\sum_j g_j}{\Phi_*}) \theta_i dx \equiv G_i(\sum_j g_j, \theta_i) , \quad (11)$$

$$\theta_i = \exp(-f_{*i} \frac{n_\infty}{\eta_{tot\ i}} \int_0^z \exp(-\Gamma_i \frac{\sum_j g_j}{\Phi_*}) dx) \equiv S_i(\sum_j g_j) , \quad (12)$$

where $f_{*i} = J_i(\eta_{tot\ i}, \Phi_*) \tau / \Phi_* \alpha n_\infty$. These equations form the closed system of the condensation equations. This system will be the subject of investigation.

For the quasi-continuous case one can use the value of activity w as an argument instead of the lower index for the sort of heterogeneous centers and get more general approximation which covers also the dependence over activity

$$f_\zeta(\zeta(x), w) = f_\zeta(\Phi_*, w) |_{w=0} \exp(\Gamma \frac{(\zeta - \Phi_*)}{\Phi_*}) \exp(w\lambda) , \quad (13)$$

where

$$\Gamma(w) = -\Phi_* \frac{d\Delta F(\zeta, w)}{d\zeta} |_{\zeta=\Phi_*} . \quad (14)$$

The dependence of Γ on w is rather weak and one can put

$$\Gamma(w) = \Gamma |_{w=0} \quad (15)$$

for some essential part of activities spectrum. What is the term "essential part of activities spectrum" will be clear later.

With the help of the conservation laws for heterogeneous centers and for molecules of the substance one can get for g, θ

$$g(z, w) = f_* \int_0^z (z-x)^3 \exp(-\Gamma \frac{g^{tot}}{\Phi_*}) \theta(x, w) dx \eta_{tot}(w) \exp(w\lambda) \equiv G_w(g^{tot}, \theta) , \quad (16)$$

$$g^{tot} = \int dw g(z, w) , \quad (17)$$

$$\theta(z, w) = \exp(-f_* \exp(\lambda w) n_\infty \int_0^z \exp(-\Gamma \frac{g^{tot}}{\Phi_*}) dx) \equiv S_w(g^{tot}) , \quad (18)$$

where $f_* = f_\zeta(\Phi_*, w = 0)$.

⁷Here the first statement is used.

The droplets size spectrum can be found as

$$f(x, w) = f_* \exp(\lambda w) \exp(-\Gamma \frac{\int dw g(x, w)}{\Phi_*}) \theta(x, w) \eta_{tot}(w) \quad , \quad (19)$$

$$f_i = f_* \exp(-\Gamma_i \frac{\sum_j g_j}{\Phi_*}) \theta_i \quad . \quad (20)$$

Since the accuracy of the theory is measured in the terms of the error in the droplets number N_i , these values are defined as

$$N_i = \eta_{tot} (1 - \theta_i(z)) \equiv Q_i(\theta_i) \quad . \quad (21)$$

The structure of further constructions will be the following

- At first the asymptotic cases will be investigated. It will be done for two types of heterogeneous centers. The generalization for many types of centers is evident and trivial. Here it isn't assumed that Γ_i don't depend on i .
- Then the general intermediate situation will be constructed with the help of approximation $\Gamma_i = const$ for all sorts of centers. One can prove that this intermediate situation and the asymptotic cases cover all possible situations.
- Then the case of the quasi continuous spectrum of the heterogeneous centers activities will be considered. Here one can use some more elegant approaches which will lead to more compact results.

3 Asymptotic solutions

3.1 Formal generalization of iteration method

At first one has to show that the case under consideration can not be reduced to trivial generalization of known approaches. The formal generalization of the iteration method analogous to [28] for the condensation on one given sort of heterogeneous centers leads to the following equations:

$$g_{i(l+1)} = G_i(\sum_j g_{j(l)}, \theta_{i(l)}) \quad , \quad \theta_{i(l+1)} = S_i(\sum_j g_{j(l)}) \quad , \quad N_{i(l)} = Q_i(\theta_{i(l)}) \quad , \quad (22)$$

$$g_{i(0)} = 0 \quad , \quad \theta_{i(0)} = 1 \quad , \quad (23)$$

$$g_{i(1)} = f_* \frac{z^4}{4} \quad , \quad \theta_{i(1)} = \exp(-f_* \frac{n_\infty}{\eta_{tot} i} z) \quad , \quad (24)$$

$$N_{i(2)}(\infty) = \eta_{tot} i [1 - \exp(-f_* \frac{n_\infty}{\eta_{tot} i} (\sum_j \frac{\Gamma_i f_{*j}}{4\Phi_*})^{-1/4} A)] \quad , \quad A = \int_0^\infty \exp(-x^4) dx \approx 0.9 \quad . \quad (25)$$

The third iteration can not be calculated in the analytical form.

Let us analyze $N_{i(2)}(\infty)$. Assume that ζ is fixed and for some i and j

$$f_{*i} \gg f_{*j} \quad .$$

Let us decrease $\eta_{tot\ i}$ and $\Delta_i F$ keeping the constant value of $f_{*i} \sim \eta_i \exp(-\Delta_i F)$. It is obvious that when $\eta_{tot\ i}$ is small then the total number of the heterogeneously formed droplets coincides with the total quantity of heterogeneous centers and goes to zero when $\eta_{tot\ i}$ goes to zero. The value of g_i at the end of the period of the droplets formation on the heterogeneous centers of the sort "j" can be estimated as

$$g_i \leq \frac{\eta_{tot\ i} (\hat{\Delta}x_j)^3}{n_\infty} ,$$

where $\hat{\Delta}x_j$ is the width of the size spectrum (of the size distribution function) for the droplets of the sort "j". The value of $\hat{\Delta}x_j$ is restricted from above by the value Δx_j which is the width of the size spectrum without any influence of the droplets of the other sorts and without any exhaustion of the heterogeneous centers of this sort. Then the influence of the heterogeneous centers of the sort i on the process of the condensation on the centers of the sort j becomes negligible in the limit $\eta_{tot\ i} \rightarrow 0$. At the same time (25) shows that in the limit $\eta_{tot\ i} \rightarrow 0$, $f_{*i} = const$ the influence of the droplets of the sort i doesn't become small. This leads to the big error for $N_j(\infty)$ in the second approximation.

One can not get an analytical expression in the third approximation for N_i in frames of the standard iteration method and the second iteration gives the wrong qualitative results. This is the main disadvantage of the standard iteration procedure. The reason for this disadvantage is the following one. Consider the situation with one type of centers. In the case when the interruption of the embryos formation is caused by exhaustion of heterogeneous centers the error in the value of g_i is compensated by the squeezing force of the operator S_i . The analogous property is absent for the operator Q_i in the situation with several types of centers due to the cross influence of the droplets formed on different sorts. This shows that the situation with several types of centers can not be effectively described by a formal generalization of the already known methods.

3.2 Characteristic lengths

The direct generalization of the iteration method fails due to the wrong account of the cross influence of the droplets formed on different sorts. Nevertheless it allows to get the spectrum of the droplets when the cross influence is excluded.

On a base of the first iterations in the general procedure one can see that for a separate process there are two characteristic lengths. The first one is the length of spectrum in the situation when there are no exhaustion of the heterogeneous centers (and no droplets of the other sort). One can say that the condensation occurs in the pseudo-homogeneous way. For this characteristic value

$$\Delta_i x = \left(\frac{4\Phi_*}{\Gamma_i f_{*i}} \right)^{1/4} . \quad (26)$$

This length is going from the first iteration for g_i . The second length is the length of the spectrum the spectrum is formed only by exhaustion of heterogeneous centers. Then the width of the spectrum is

$$\delta_i x = \frac{\eta_{tot\ i}}{f_{*i} n_\infty} . \quad (27)$$

This length is going from the first iteration for θ_i .

Practically the hierarchy between $\Delta_i x$ and $\delta_i x$ is ensured by the hierarchy between f_{*i} and η_{*i} . The values of Γ_i are rather (in comparison with f_{*i}) unsensible to the value of the supersaturation. Really

$$-\frac{\Gamma_i}{\zeta} = \frac{d\Delta_i F}{d\zeta} \sim \frac{dF_{i,c}}{d\zeta} - \frac{dF_{i,e}}{d\zeta} . \quad (28)$$

The value $dF_{i,c}/d\zeta$ can be estimated from above by the value in the limit of homogeneous condensation $dF_{c,hom}/d\zeta$ when the force of interaction between the heterogeneous center and molecules of liquid decreases monotonously in space. Since the energy of the solvation⁸ depends on the supersaturation weaker than F_c depends, one can neglect the last term of the previous equation and get

$$\frac{d\Delta F}{d\zeta} \sim \frac{dF_{c,hom}}{d\zeta} . \quad (29)$$

This dependence is rather weak in comparison with a very sharp dependence of f_{*i} on the supersaturation.

Another important fact is the frontal form of a back side of spectrum⁹ in the pseudo-homogeneous situation (when Γ_i really plays an important role)¹⁰. The frontal character can be seen from

$$f_i = f_{*i} \exp\left(-\frac{\Gamma_i}{4\Phi_*} \left(\sum_j f_{*j}\right) z^4\right) . \quad (30)$$

A moderate variation of $\Delta_i x$ can be caused only by a very big variation of f_{*i} .

Instead of $\delta_i x$ one can use parameter

$$h_i = \frac{\delta_i x}{\Delta_i x} \quad (31)$$

to simplify formulas.

Now one can directly analyze all asymptotic cases.

3.3 The case $\Delta_1 x \sim \Delta_2 x$

3.3.1 Situation $h_1 \ll 1, \quad h_2 \geq 1$

In this situation

- The process of formation of the droplets on heterogeneous centers of the first sort doesn't depend on formation of the droplets of the second sort.

It can be directly seen from the chain of inequalities

$$\delta_1 x \ll \Delta_1 x \sim \Delta_2 x \leq \delta_2 x . \quad (32)$$

So, the process of formation of the first sort droplets is described by the following equalities:

$$g_1 = f_{*1} \int_0^z (z-x)^3 \exp\left(-\Gamma_1 \frac{g_1(x)}{\Phi_*}\right) \theta_1 dx \equiv G_1(g_1, \theta_1) , \quad (33)$$

⁸Under barrier character of condensation, i.e. when $\Delta_i F \gg 1$.

⁹The front side has evidently the front character.

¹⁰The pseudo homogeneous situation can be defined as the situation when the centers of condensation remain practically free.

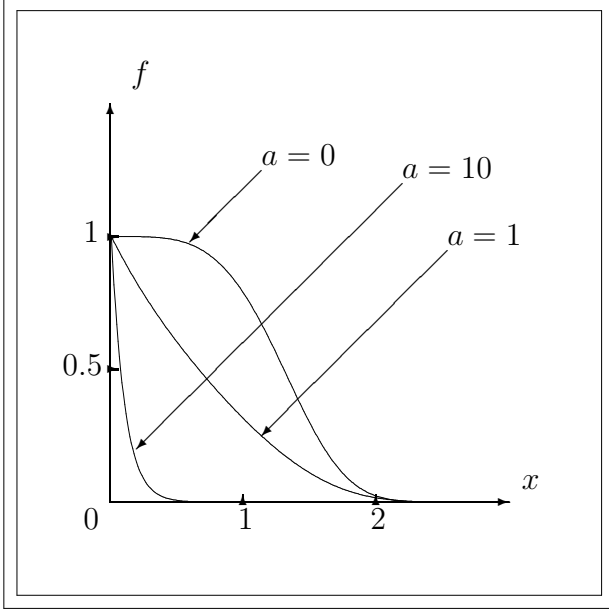


Figure 1.

Solution of the system (35) - (36). The behavior of $f = \exp(-g)\theta$ as function of x is drawn.

$$\theta_1 = \exp(-f_{*1} \frac{n_\infty}{\eta_{tot1}} \int_0^z \exp(-\Gamma_1 \frac{g_1(x)}{\Phi_*}) dx) \equiv S_1(g_1) \quad . \quad (34)$$

The system (33) - (34) can be reduced by rescaling to

$$g_1 = \int_0^z (z-x)^3 \exp(-g_1(x)) \theta_1 dx \quad , \quad (35)$$

$$\theta_1 = \exp(-a \int_0^z \exp(-\Gamma_1 \frac{g_1(x)}{\Phi_*}) dx) \quad (36)$$

with some parameter $a = f_*^{3/4} n_\infty \Phi_*^{1/4} / (\eta_{tot1} \Gamma_1^{1/4})$. Solution of the system (35)-(36) is drawn in Fig. 1 for different a .

The system (33) - (34) can be solved by the following iterations

$$g_{1(i+1)} = G_1(g_{1(i)}, \theta_{1(i)}) \quad , \quad \theta_{1(i+1)} = S_1(g_{1(i)}) \quad , \quad N_{1(i)} = Q_1(\theta_{1(i)}) \quad . \quad (37)$$

When for all values of the arguments

$$w_1 \leq w_2$$

then

$$S_1(w_1) \leq S_1(w_2) \quad .$$

When for all values of the arguments

$$w_1 \leq w_2$$

then

$$Q_1(w_1) \geq Q_1(w_2) \quad .$$

When for all values of the arguments

$$w_1 \leq w_2 \quad , \quad v_1 \geq v_2$$

then

$$G_1(v_1, w_1) \leq G_1(v_2, w_2) \quad .$$

The initial approximations can be chosen as

$$g_{1(0)} = 0 \quad , \quad \theta_{1(0)} = 1 \quad , \quad (38)$$

which leads to

$$g_{1(0)} \leq g_{1(2)} \leq \dots \leq g_{1(2i)} \leq \dots \leq g_1 \leq \dots \leq g_{1(2i+1)} \leq \dots \leq g_{1(3)} \leq g_{1(1)} \quad , \quad (39)$$

$$\eta_{1(0)} \geq \eta_{1(2)} \geq \dots \geq \eta_{1(2i)} \geq \dots \geq \eta_1 \geq \dots \geq \eta_{1(2i+1)} \geq \dots \geq \eta_{1(3)} \geq \eta_{1(1)} \quad ,$$

$$N_{1(0)} \leq N_{1(2)} \leq \dots \leq N_{1(2i)} \leq \dots \leq N_1 \leq \dots \leq N_{1(2i+1)} \leq \dots \leq N_{1(3)} \leq N_{1(1)} \quad . \quad (40)$$

These estimates allow to prove the convergence of iterations.

The calculation of iterations gives

$$g_{1(1)} = f_{*1} \frac{z^4}{4} \quad , \quad \theta_{1(1)} = \exp(-f_{*1} \frac{n_\infty}{\eta_{tot1}} z) \quad , \quad (41)$$

$$N_{1(2)}(\infty) = \eta_{tot1} (1 - \exp(-f_{*1} \frac{n_\infty}{\eta_{tot1}} (\frac{\Gamma_1}{4\Phi_*})^{-1/4} f_{*1}^{-1/4} A)) \quad . \quad (42)$$

Since

$$\frac{d}{dx} |N_{1(i)} - N_{1(j)}| \geq 0 \quad , \quad (43)$$

by the simple numerical calculation of $N_{1(3)}(\infty)$ one can see

$$\frac{|N_{1(2)} - N_1|}{N_1} \leq 0.015 \quad ,$$

which means that the second iteration is already rather precise¹¹.

On the base of the iterations one can get some approximations for the supersaturation¹²:

$$\zeta_{(l+1)} = \Phi_* - f_{*1} \int_0^z (z-x)^3 \exp(-\Gamma_1 \frac{g_{1(l)}}{\Phi_*}) \theta_{1(l)} dx \quad (44)$$

and come to the second approximation for ζ

$$\zeta_{(2)} = \Phi_* - f_{*1} \int_0^z (z-x)^3 \exp(-Hx) dx = \Phi_* + f_{*1} [-\frac{z^3}{H} + \frac{3z^2}{H^2} - \frac{6z}{H^3} + \frac{6}{H^4} \exp(-Hz)] \quad , \quad (45)$$

where

$$H = \frac{f_{*1} n_\infty}{\eta_{tot1}} \quad (46)$$

¹¹The same procedure can be used for the condensation on one sort of heterogeneous centers.

¹²Without the second sort droplets taken into account.

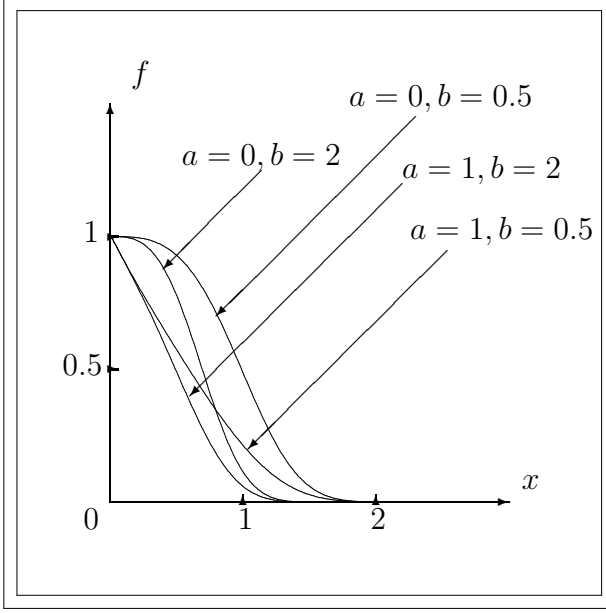


Figure 2.

Solution of the system (50) - (51). The behavior of $f = \exp(-g)\theta$ as function of x is drawn.

This expression can be simplified. The value of supersaturation appears in expression for the size spectrum $f(x)$ in the form $\exp(-\Gamma_i(\zeta - \Phi_*)/\Phi_*)$. After the substitution of $\zeta_{(2)}$ into this expression one can see that in the case when ζ deviates essentially (i.e. when the exponent changes) from Φ_* all terms except the first two ones can be neglected and

$$\zeta_{(2)} = \Phi_* - z^3 \frac{\eta_{tot\ 1}}{n_\infty} . \quad (47)$$

For the second sort one can obtain the following system of equations

$$g_2 = f_{*2} \int_0^z (z-x)^3 \exp(-\Gamma_2 \frac{g_2(x) + (\eta_{tot\ 1}/n_\infty)x^3}{\Phi_*}) \theta_2 dx \equiv G_2(g_2 + (\eta_{tot\ 1}/n_\infty)x^3, \theta_2) , \quad (48)$$

$$\theta_2 = \exp(-f_{*2} \frac{n_\infty}{\eta_{tot\ 2}} \int_0^z \exp(-\Gamma_2 \frac{g_2(x) + (\eta_{tot\ 1}/n_\infty)x^3}{\Phi_*}) dx) \equiv S_2(g_2 + (\eta_{tot\ 1}/n_\infty)x^3) . \quad (49)$$

This system can be rescaled to

$$g_2 = \int_0^z (z-x)^3 \exp(-g_2(x) - bx^3) \theta_2 dx , \quad (50)$$

$$\theta_2 = \exp(-a \int_0^z \exp(-g_2(x) - bx^3) dx) \quad (51)$$

with constants $a = f_{*2}^{3/4} n_\infty \Phi_*^{1/4} / (\eta_{tot\ 2} \Gamma_2^{1/4})$ and $b = \eta_{tot\ 2} \Gamma_2^{3/4} / (n_\infty \Phi_*^{3/4} f_{*2}^{1/4})$. Solutions of this system for different values of a and b are shown in Fig. 2.

Having introduced

$$\lambda_2 = g_2 + (\eta_{tot\ 1}/n_\infty)z^3 \ , \quad (52)$$

one can rewrite the system (48)-(49) as

$$\lambda_2 = G_2(\lambda_2, \theta_2) + (\eta_{tot\ 1}/n_\infty)z^3 \equiv G_2^+(\lambda_2, \theta_2) \ , \quad (53)$$

$$\theta_2 = S_2(\lambda_2) \ . \quad (54)$$

The operator G_2^+ has the same properties as G_1, G_2 have. All chains of inequalities remain valid with the index "2" instead of "1" and the operator G_2^+ instead of G_2 . Moreover one can see that

$$\frac{d}{d(\eta_{tot\ 1}/n_\infty)} |N_{2\ (i)} - N_{2\ (j)}| \leq 0 \ , \quad (55)$$

which shows that the worst situation for the iterations convergence is $\eta_{tot} = 0$. Even in this situation the second iteration is rather precise. It can be seen from investigation of nucleation on the first sort of centers.

Actually one can avoid here the calculations according to such a complex procedure. The term $\eta_{tot\ 1}z^3/n_\infty$ ensures the characteristic length

$$D_1 = \left(\frac{\Phi_* n_\infty}{\Gamma_2 \eta_{tot\ 1}} \right)^{1/3} \ . \quad (56)$$

Since

$$D_1 \geq \epsilon \Delta_1 x \sim \epsilon \Delta_2 x \quad \epsilon \sim (2 \div 3) \ , \quad (57)$$

the condensation on the centers of the second sort occurs in the separate way, the influence of the first sort of centers here is negligible and one can use the formulas (33)-(37), (41)-(43) with the index "2" instead of the index "1".

3.3.2 Situation $h_1 \geq 1, \quad h_2 \ll 1$

Since $\Delta_1 x \sim \Delta_2 x$, one can change the numbers of sorts and reduce this situation to the previous one.

3.3.3 Situation $h_1 \geq 1, \quad h_2 \geq 1$

To analyze this situation one has to understand why in the separate condensation on one sort already the second iteration gives rather precise results. This property is explained by the big power 3 in the subintegral expression for g_i . Then the droplets of the big sizes near the front side of the spectrum are the main consumers of the vapor. These droplets have small (in comparison with $\Delta_i x$) values of the variable x . The cross influence is rather weak and one can use the general iteration procedure which gives

$$g_{i\ (1)} = f_{*i} \frac{z^4}{4} \ , \quad i = 1, 2 \ , \quad (58)$$

$$\theta_{i\ (1)} = \exp(-f_{*i} \frac{n_\infty}{\eta_{tot\ 1}} z) \ , \quad (59)$$

$$N_{i(2)}(\infty) = \eta_{tot\ i} [1 - \exp(-f_{*i} \frac{n_\infty}{\eta_{tot\ i}} ((\frac{\Gamma_i}{4\Phi_*}) f_{*1} + (\frac{\Gamma_i}{4\Phi_*}) f_{*2})^{-1/4} A)] . \quad (60)$$

Since the exhaustion of heterogeneous centers is moderate, the precision of iterations resembles the homogeneous case and allows the estimate $|N_{i(2)} - N_i| < 0.15N_i$.

3.3.4 Situation $h_1 \ll 1, h_2 \ll 1$

Since

$$\delta_1 x \ll \Delta_1 x \sim \Delta_2 x , \quad (61)$$

the droplets of the second sort don't act on the process of formation of the droplets of the first sort. Since

$$\delta_2 x \ll \Delta_2 x \sim \Delta_1 x , \quad (62)$$

the same is valid for the droplets of the second sort. The system is split into parts corresponding to the separate processes of the condensation on different sorts. Eq. (33)-(37) can be reproduced here. But in the case $h_i \ll 1$ for all i the vapor exhaustion can be neglected in comparison with the exhaustion of heterogeneous centers and one can get precise explicit results

$$\theta_i(x) = \exp(-f_{*1} \frac{n_\infty}{\eta_{tot\ 1}} z) , \quad i = 1, 2 , \quad (63)$$

$$f_i(x) = f_{*i} \exp(-f_{*i} \frac{n_\infty}{\eta_{tot\ i}} z) , \quad (64)$$

$$\zeta = \Phi_* - (\frac{\eta_{tot\ 1}}{n_\infty} + \frac{\eta_{tot\ 2}}{n_\infty}) z^3 . \quad (65)$$

This expression for ζ is obtained by the same procedure as that which led to (47).

3.4 Case $\Delta_1 x \ll \Delta_2 x$

Due to $\Delta_1 x \ll \Delta_2 x$ the droplets of the second sort don't act on the process of formation of the droplets of the first sort. The process¹³ of formation of the droplets of the first sort can be described by the iteration procedure presented by eq.(37).

3.4.1 Situation $h_1 \ll 1, h_2 \geq 1$

Due to $h_1 \ll 1$ the equation for g_1 can be simplified

$$g_1 = f_{*1} \int_0^z (z-x)^3 \exp(-Hx) dx \sim \frac{\eta_{tot\ 1}}{n_\infty} z^3 . \quad (66)$$

The value of θ_1 is given by (63), the value of $f_1(x)$ is given by (64).

For the condensation on the centers of the second sort the equations analogous to (48),(49) are suitable. So, one can get here equations (52)-(55). But in this situation the inequality (57) isn't valid and one must calculate iterations. One can choose as initial approximation $\lambda_{2(0)} = 0$ and get

$$\lambda_{2(1)} = f_{*2} \frac{z^4}{4} + \frac{\eta_{tot\ 1}}{n_\infty} z^3 , \quad (67)$$

¹³The case $\Delta_2 x \gg \Delta_1 x$ is reversal to this case and can be considered by the simple change of the indexes.

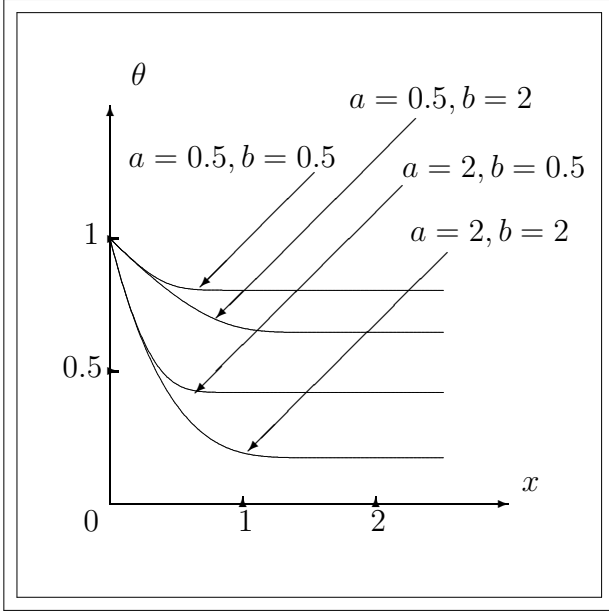


Figure 3.
Behavior of θ as function of x for different a, b .

$$\theta_{2(2)} = \exp(-f_{*2} \frac{n_{\infty}}{\eta_{tot2}} \int_0^z \exp(-(\frac{x}{\Delta_{\infty 2x}})^4 - (\frac{x}{\Delta_{h1x}})^3) dx) , \quad (68)$$

where

$$\Delta_{\infty 2x} = (\frac{4\Phi_*}{\Gamma_2 f_{*2}})^{1/4} \equiv \Delta_{2x} , \quad \Delta_{h1x} = (\frac{\Phi_* n_{\infty}}{\Gamma_2 \eta_{tot1}})^{1/3} \equiv D_1 .$$

Eq. (68) can be rescaled to

$$\theta_{2(2)} = \exp(-a \int_0^z \exp(-x^4 - bx^3) dx) \quad (69)$$

with parameters $a = f_{*2} n_{\infty} \Delta_{\infty 2x} / \eta_{tot2}$ and $b = (\Delta_{\infty 2x})^3 / (\Delta_{h1x})^3$. This dependence is shown in Fig. 3.

The value of $\Delta_{\infty 2x}$ has the sense of the spectrum width when the cross influence and the exhaustion of heterogeneous centers are neglected. The value of Δ_{h1x} has the sense of the spectrum width when the vapor consumption by droplets is neglected.

One can easily prove that

$$\frac{d}{dx} |N_{2(i)} - N_{2(j)}| \geq 0 , \quad \frac{d}{d\eta_{tot1}} |N_{2(i)} - N_{2(j)}| \leq 0$$

for $i, j \geq 2$. Then it is easy to show that

$$\frac{|N_{2(2)} - N_2|}{N_2} \leq 0.015$$

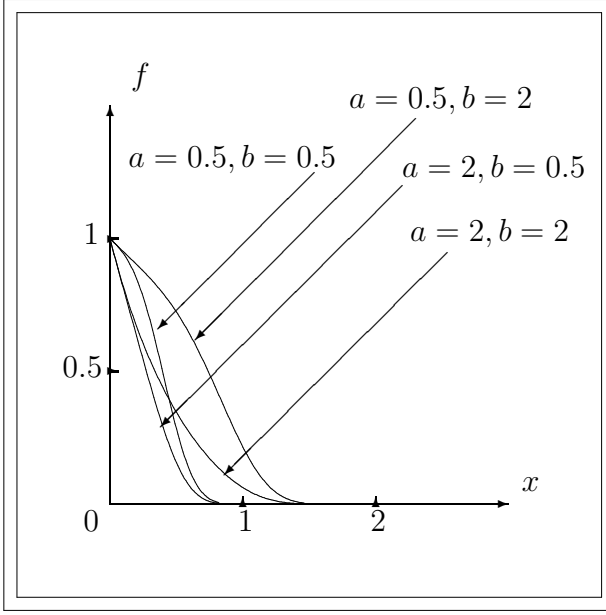


Figure 4.
The form of the size spectrum.

by the calculation of $N_{2(2)}(\infty)$ and $N_{2(3)}(\infty)$ at $\eta_{tot\ 1} = 0$.

The simple approximation can be obtained if one notices that on the base of (68)

$$\theta_{2(2)}(\infty) \approx \exp[-f_{*2}\Delta_{\infty 2x}\frac{n_{\infty}}{\eta_{tot\ 2}}(\frac{A}{2}(1+(\frac{\Delta_{\infty 2x}}{\Delta_{h\ 1x}})^4)^{-1/4} + \frac{B}{2}(1+(\frac{\Delta_{\infty 2x}}{\Delta_{h\ 1x}})^3)^{-1/3}]] \quad , \quad (70)$$

where

$$B = \int_0^{\infty} \exp(-x^3)dy \quad ,$$

with the relative error less than 0.035.

The spectrum of sizes of the droplets formed on the centers of the second sort is

$$f_2 = f_{*2} \exp(-\frac{\Gamma_2 f_{*2}}{\Phi_*} \frac{z^4}{4}) \exp(-\frac{\Gamma_2}{\Phi_*} \frac{\eta_{tot1}}{n_{\infty}} z^3) \exp(-f_{*2} \frac{n_{\infty}}{\eta_{tot\ 2}} \int_0^z \exp(-(\frac{x}{\Delta_{\infty 2x}})^4 - (\frac{x}{\Delta_{h\ 1x}})^3) dx) \quad . \quad (71)$$

By appropriate rescaling it can be reduced to

$$f_2 \sim \exp(-z^4) \exp(-(\frac{z}{b})^3) \exp(-a \int_0^z \exp(-x^4 - (\frac{x}{b})^3) dx) \quad (72)$$

with two parameters $a = f_{*2} n_{\infty} \Delta_{\infty 2x} / \eta_{tot\ 2}$ and $b = \Delta_{h\ 1x} / \Delta_{\infty 2x}$ which is drawn in Fig.4.

3.4.2 Situation $h_1 \geq 1, h_2 \ll 1$

The description of the process of formation of the droplets of the first sort can't be simplified. It has been already given in the previous sections. But the process of formation of the droplets

of the second sort is rather simple to describe. The supersaturation is determined by the vapor consumption by the droplets of the first sort. Then one has the following expressions

$$\theta_2 = \exp(-f_{*2} \frac{n_\infty}{\eta_{tot2}} \int_0^z \exp(-\Gamma_2 \frac{g_1}{\Phi_*}) dx) , \quad (73)$$

$$g_2 = f_{*2} \int_0^z (z-x)^3 \exp(-\Gamma_2 \frac{g_1}{\Phi_*}) \theta_2 dx . \quad (74)$$

The value of g_2 during the period of the nucleation on the centers of the second sort can be estimated as

$$g_2 \ll \frac{\Phi_*}{\Gamma_2} ,$$

which is based on

$$\delta_2 x \ll \Delta_2 x .$$

So, g_2 is negligible. It is necessary to calculate only θ_2 . To calculate θ_2 one can get into account that the value of g_1 grows so rapidly that for the value of $\int_0^z \exp(-\Gamma_2 \frac{g_1}{\Phi_*}) dx$ one can show the following approximation

$$\int_0^z \exp(-\Gamma_2 \frac{g_1}{\Phi_*}) dx \approx z \Theta(1 - \frac{\Gamma_2 g_1}{\Phi_*}) + \int_0^\infty \exp(-\Gamma_2 \frac{g_1}{\Phi_*}) dx \Theta(\frac{\Gamma_2 g_1}{\Phi_*} - 1) ,$$

or

$$\int_0^z \exp(-\Gamma_2 \frac{g_1}{\Phi_*}) dx \approx z \Theta(1 - \frac{\Gamma_2 g_1}{\Phi_*}) + z_b \Theta(\frac{\Gamma_2 g_1}{\Phi_*} - 1) ,$$

where z_b is extracted by the condition

$$g_1(z_b) = \frac{\Phi_*}{\Gamma_2}$$

and Θ is the Heavisaid function. The last approximation allows to calculate θ_2 analytically.

3.4.3 Situation $h_1 \geq 1, h_2 \geq 1$

Actually, this situation has been already analyzed in description of the situation $\Delta_1 x \ll \Delta_2 x; h_1 \geq 1, h_2 \ll 1$. Since $\Delta_1 x \ll \Delta_2 x$ one could not effectively use there the condition $h_2 \ll 1$ because one could not assume that the inequality $h_2 \ll 1$ ensures the pure exhaustion of heterogeneous centers without any vapor exhaustion and the consideration made earlier couldn't be simplified. As the result the previous consideration covers the situation $h_1 \geq 1, h_2 \geq 1$.

3.4.4 Situation $h_1 \ll 1, h_2 \ll 1$

From the first point of view it seems that the situation $h_1 \ll 1, h_2 \ll 1$ has been already described. One has to stress that $h_i \ll 1$ doesn't allow to state that the nucleation process is going at the constant value of the supersaturation. For the first sort nucleation one has the previous expressions (63), (64). The analogous expressions (63), (64) for the second sort nucleation can be violated. So, the process of nucleation of the second sort droplets can not be described on the base of the initial value of the supersaturation.

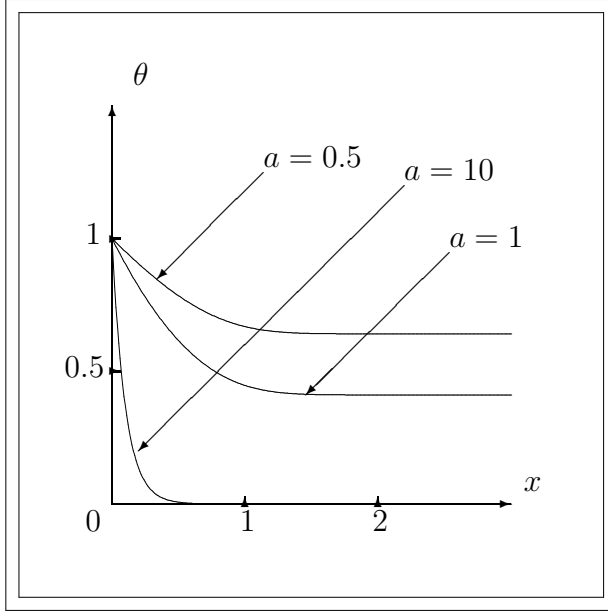


Figure 5.
Function $\theta_{2(2)}(x)$ for different a .

The calculation of g_2 isn't necessary and only the calculation of θ_2 is essential. One has

$$\theta_{2(2)} = \exp\left(-f_{*2} \frac{n_\infty}{\eta_{tot2}} \int_0^z \exp\left(-\left(\frac{x}{\Delta_{h1}x}\right)^3\right) dx\right), \quad (75)$$

the final value for θ_2 can be given by

$$\theta_{2(2)}(\infty) = \exp\left[-f_{*2} \Delta_{h1}x \frac{n_\infty}{\eta_{tot2}} B\right]. \quad (76)$$

Eq. (75) can be reduced by the simple rescaling to

$$\theta_{2(2)} = \exp\left(-a \int_0^z \exp(-x^3) dx\right) \quad (77)$$

with parameter $a = f_{*2} n_\infty \Delta_{h1}x / \eta_{tot2}$. This behavior is drawn in Fig. 5.

The mono-disperse approximation for the size spectrum of the first sort droplets is based on the evident chain of the inequalities

$$\hat{\Delta}x_1 \sim \delta_1x \ll \Delta_1x \ll \Delta_2x.$$

When the mono-disperse approximation fails then the vapor consumption isn't essential at all.

Now all imaginary possible asymptotic situations have been studied. It doesn't mean that all of them take place for two given sorts of heterogeneous centers and some given substance.

The second part of the manuscript which can be found in the cond-mat e-print archive at the same publishing date will complete the theory.

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